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CHLORINATED SOLVENTS DETECTION IN SOIL AND RIVER WATER IN THE AREA ALONG THE PAPER FACTORY FROM DEJ TOWN, ROMANIA

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ABSTRACT. Considerable amounts of chlorinated solvents compounds were identified and measured in raw water and soil samples collected during several month studies, along the Somes River near Dej city region of Romania. The most common organochlorine solvents detected were trichloroethylene (C_2HCl_3), tetrachloroethylene (C_2Cl_4), carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) with the range between 3.05 – 68.92 µg L^{-1}, 5.62 – 55.48 µg L^{-1}, 2.11 – 29.45 µg L^{-1} and 0.37 – 80.29 µg L^{-1}. They were detected using a mass spectrometer coupled at a gas chromatograph with electron capture detector and quantified using chlorinated solvent standards. Organochlorine compounds have different chemical properties that lead into a broad range to uses. Many of them have significant biological activities and some of them can be very toxic for plant, animals and humans. Because of that they present seriously environmental concern. This study presents the source of the pollution and also the levels of these pollutants in river water and the soil.

Keywords: chlorinated solvents, environmental pollution, GC-MS, GC-ECD.

INTRODUCTION

Starting with October 2006 it was observed in several water sample collected from Somes River Basins a high level of some chlorinated solvents. The aim of this study was to identify the chlorinated solvent species presence in river water and established the amount of them. Starting with results obtained from river water analysis was supposed also the possibility of soil contamination, so in the same time were analyzed even the soil sampled near the Somes River. Another goal of this study was to identify the possible pollution source. As shown previous medical and environmental researches, these compounds can induce serious adverse effects to humans and environment [1]. Chlorinated solvents are associated with a series of adverse human health effects such

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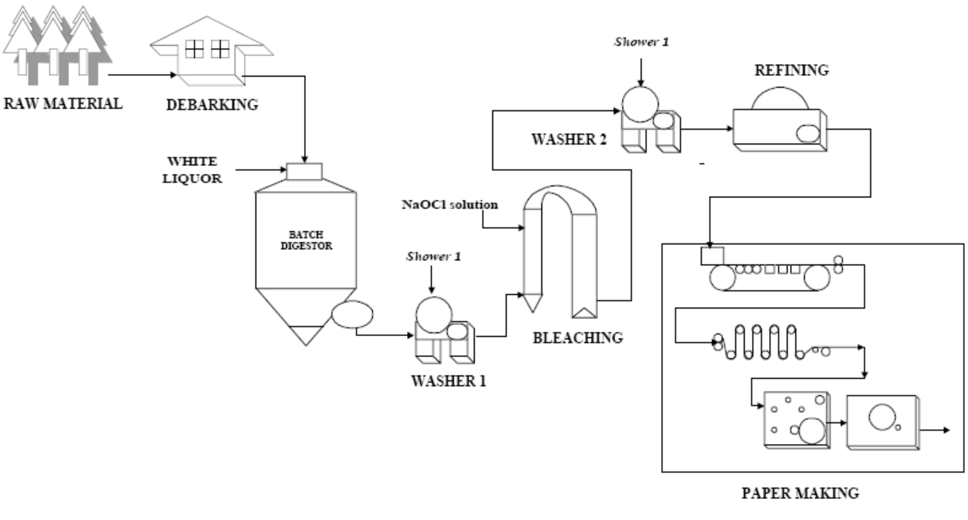
as toxicity of central nervous system, reproductive, liver and kidney and also carcinogenicity [2 - 5]. Several chlorinated solvents are used in large volume amount in industry because they own a batch proper chemical and physical property [6 - 9]. They are widely used as solvents for fats, oils, waxes and resins or adhesives solvent, in dry cleaning operations, cleaning printed circuit boards, vapour degreasing, parts cleaning, engine cleaner or degreasing agent and paint remover. Many times they are used primarily to produce other chemicals or as chemical intermediate, also are used in organic synthesis, fluorocarbon and polymer manufacture, aerosol propellant and foam plastic blowing agents.

Dej is a small city located at 60 km from Cluj-Napoca town where Somesul Mic River meet Somesul Mare River. At the outlying of Dej city is water making factory. It is known as the pulp and paper industry has been consuming much water. The simple process of paper making is almost the same as the method of Cailun who is the invitatory of paper in ancient China. In Dej paper making factory, the Kraft process is the main process applied in the paper production. The main chemicals are sodium hydroxide (NaOH) for pulping and chlorine for bleaching. The production of paper can be divided in seven steps: a. raw material selection and preparation; b. digestion; c. washing; d. bleaching; e. washing; f. refining or beating and g. paper making – as shown in scheme 1. This paper making unit (g) consists of many unit operations such as: sheet forming, transferring, pressing, and drying. Finally is obtained the paper.



Scheme 1

RESULTS AND DISCUSSION

Organochlorine are organic compounds and from it class make part chlorinated solvents. Some of chlorinated solvents are volatile organic compounds. The most common organochlorine and chlorinated solvents founded in Somes river water were: carbon tetrachloride, 1,2-dichloroethane, 1,1-dichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, methylene chloride, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, vinyl chloride and chloroform, dichlorobromomethane, dibromochloromethane.

Chlorinated solvents are widely used in industry such as in the paper making factory and also in common household products. These chemicals are used as degreasing fluids for many different purposes such as dry-cleaning clothes, de-caffeinate coffee, cleaning metal machinery, dissolving grease build up in septic tanks and in making paper industry.

Because some of the organochlorine compounds are volatile organic compounds (VOCs) they can move easily through the environment. If improperly discarded onto the ground, these chemicals can travel downward through the soil and eventually end up in the groundwater. Organochlorine compounds such as chloroform, trichloroethylene or tetrachloroethene are not usually found in river water because they tend to evaporate from the water into the air but they can appear in river just if exist a source of man made pollution. Even that in all sample collected from Somes River was found such of kind's organochlorine compounds and in the high concentration level. That could de explain by the fact that near the Somes River outlying Dej district is located the paper factory where in the paper making process is used high amount of chlorine based solvents. Actually in the bleaching steps from the paper making process – where the purposes of this process are to whiten the pulps is used high amount of organochlorine solvents. In that process unbleached pulps are loaded to the bleaching tanks (see scheme 1), the common bleaching chemicals used normally are sodium hypochlorite or calcium hypochlorite. Also in the washing steps the bleacher bark is transferred to the concrete tanks for washing. This washing steps in performed 2 - 5 times or until the smell of chlorine disappears. The factory evacuates that water in Somes River. It was observed that after the closing of factory for two weeks the concentration level of these compounds started to decreased – table1.

When the factory was closed organochlorine compounds concentration was followed every day in the water sample during October. In the middle of the month the factory was closed (in 15 October the factory was closed to 28 October when the factory was opened again). Our measurement show that the concentration for the followed compounds started to decreased after the factory was closed. Before the concentration for chloroform was between 65 – 85 μg/l and after that the factory was closed the concentration was between 35 – 55 μg/l – see figure 1. The same situation was observed for trichloroethylene and tetrachloroethene, their concentration decreasing with 30 -50 %, after that the factory was closed.

Table 1. Chloroform and trichloroethylene concentration variation when factory are working on and after that the factory was closed

Observation	Data of sampling	$CHCl_3$ $\mu g\ L^{-1}$	C_2HCl_3 $\mu g\ L^{-1}$
Factory on working	1	77.42	66.79
	2	78.65	48.59
	3	68.88	56.73
	4	61.26	50.12
	5	65.94	55.08
	6	66.05	57.49
	7	71.19	49.37
	8	79.05	69.28
	9	78.01	66.35
	10	79.53	68.11
	11	80.42	52.94
	12	86.79	48.97
	13	88.29	54.26
	14	87.41	54.92
	15	85.23	51.05
Factory are closed	16	76.48	44.11
	17	68.99	42.68
	18	60.27	35.16
	19	54.29	29
	20	59	11.59
	21	53.84	24.61
	22	54.59	30.94
	23	58.93	22
	24	49.02	21.54
	25	52.61	13.98
	26	43.27	10
	27	38.75	14.29

It is known that are several natural sources that may contribute significantly to the chlorocarbons in the environment [8]. For example chloroform is a major contributor to natural gaseous chlorine. It was found to be emitted by several anthropogenic and natural sources including the terrestrial areas. The origin of chloroform in the terrestrial environment can be anthropogenic point sources, atmospheric deposition, released by vegetation and production directly in the soil. Among terrestrial sources, forest has recently been identified as contributing to the release of chloroform into the environment [9]. But in our case it was found that the major chlorinated compounds detected in the Somes river are industrial origin alone, once due the factory that evacuate the dirty used water directly in the river and on the other hand due to atmospheric pollution that is an important source of contamination of surface water and soil by rain [9].

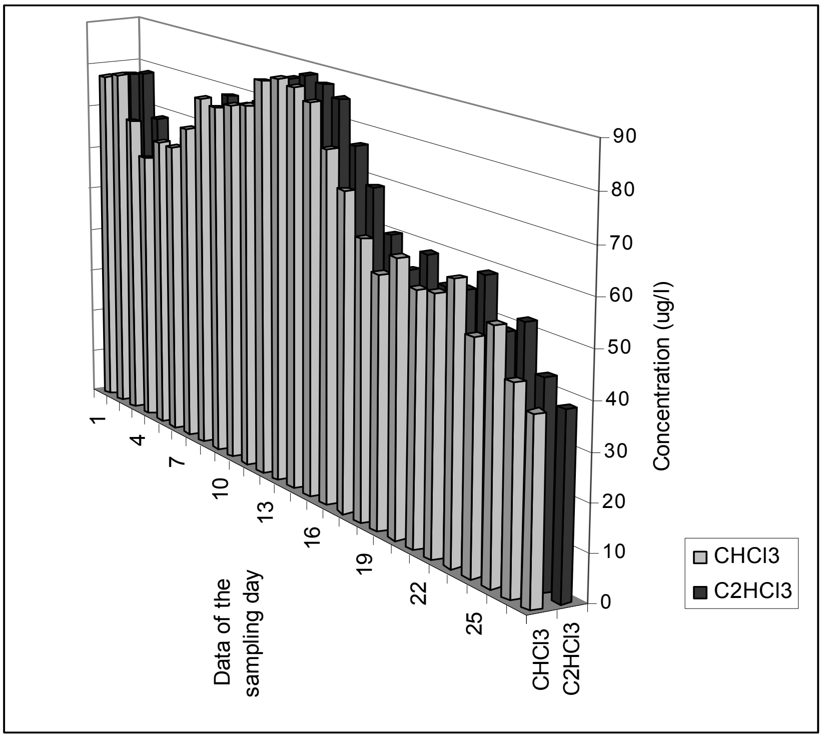


Figure 1. Trichloroethylene (C_2HCl_3) concentration (µg L^{-1}) and $CHCl_3$ concentration (µg L^{-1}) measured in Somes river water sample in October when the paper factory was working and after that the factory was closed.

In analysis of the water sample and soil sample the main found organochlorine were chloroform, TCE and PCE (see table 2 and 3). The presence of chloroform in terrestrial natural sources is still poorly investigated.

Table 2. Chloroform, trichloroethene and tetrachloroethene concentration value (µg/l) during May – October 2007 from soil sample from Dej sampling point.

Month	Chloroform (µg/l)	Trichloroethylene (µg/l)	Tetrachloroethylene (µg/l)
May	57.92	36.09	27.66
June	66.29	33.26	54.37
July	79.5	52.1	76.28
August	86.22	44.68	69.45
September	74.92	43.95	35.82
October	43.95	29.41	39

Table 3. Chloroform, trichloroethylene and tetrachloroethene concentration value (μg/l) during May – October 2007 from raw water sample.

Month	Chloroform (μg/l)	Trichloroethylene (μg/l)	Tetrachloroethylene (μg/l)
May	22.14	25.09	18.26
June	15.92	28.71	34.08
July	28.34	18.44	42.08
August	19.05	37.09	44.51
September	11.53	28.69	27.63
October	14.02	19.48	20.49

The formation and emission of chloroform by forest soil and observed large variation seen between sampling areas to the question of whether a seasonal variation exist (see figure 2 and 3). This may be expected if the production is biologically catalyzed.

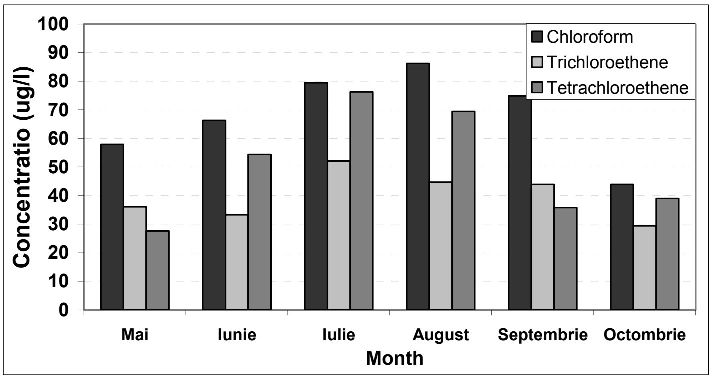


Figure 2. Chloroform, trichloroethene and tetrachloroethene variation during May – October 2007 from soil sample.

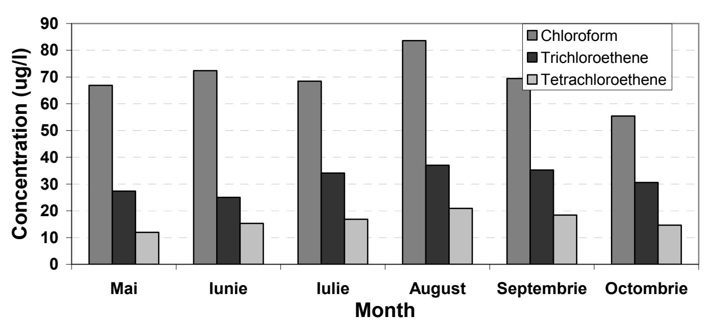


Figure 3. Chloroform, trichloroethene and tetrachloroethene variation during May – October 2007 from surface water sample.

CONCLUSIONS

The measurements of the Somes river water samples have shown that the industrial pollution is the most important sources of the chloroform, trichloroethylene and tetrachloroethene in the environment.

The major identified organocglorine compounds in the water and soil sample was chloroform, trichloroethen and tetrachloroethene. The presence of TCE and PCE can be explained by human hand made pollution of the environmental especially in Dej city where in the sample were measured higher concentration of this compounds. That could be caused from the factory that leased the used water in the Somes River. Also they used in their work process substances like TCE and $CHCl_3$. But also the natural source for chloroform exists and makes a contribution to the global sources. While chloroform alone may play a minor role in the global chlorine cycle, it may play be worth considering more seriously when taken together with other naturally – produced chlorocarbons. During the different month it was observed a highly seasonally variability for that compounds. That can be explaining by the fact that when the temperature increases, reaction is faster. In the winter months it is wait to be less concentration of these compounds because in some case ice cover protects surface of raw water and soil, and in that case the concentration of TCE, PCE and $CHCl_3$ found in nature due to their anthropogenic source are lower due to lower temperature and natural organic matter.

Also the results have shown that the concentration measured for the chloroform, trichloroethylene and tetrachloroethene was high in the period when the factory was on working. After that the factory was shot down the concentration for the followed compounds start to decrease. The difference between the concentration measured in the period of function of factory and in the period when the factory was close is high (almost 50%) – see figure 1. The major pollution of the soil and waste water is due to the paper factory.

EXPERIMENTAL SECTION

Water samples: were collected in 40 mL screw cap glass vials equipped with PTFE-faced single use septa. Prior to use the vials were washed with hot soapy water then rinse thoroughly with ultrapure water. After that, all cleaned vials were dry at 200 °C for 6 – 10 hours in an oven. All water samples were collected in duplicate and preserved. Phosphate buffer were used to inhibit base catalyzed degradation of some chlorinated solvents and to standardize the pH of all samples. The buffer were prepared as a dry homogenous mixture of 1 % Na_2HPO_4/99 % KH_2PO_4, from that mixture 0.8 g were add to all 40 mL vials before sampling. Water sample or extract were store at 4 °C in a freezer until the analysis. All extracts of the samples were analyzed within 14 days after sampling. The primary dilution standard was prepared in 50 mL buffered reagent water, from it 500 μL with acetone were add in a 50 mL volumetric flask. This yields a final concentration in water of 10 μg/L and this solution were fortified into the aqueous sample prior to extraction. The chlorinated solvents were extracted from water samples with MTBE (high purity) after addition of surrogate analyte fortification solution. 10 g NaCl were add to the water sample before extraction. The NaCl/MTBE/water sample mixture was shaking vigorously and consistently by hand. After that the separator funnel was invert for 3-5 minutes to allow the water and MTBE phases to separate. 1 mL from the solvent phase was transferred to analysis vial and it analysis was done on gas chromatography equipped with an electron capture detector (GC-ECD) and splitless injector. The column used for analysis was Trace TR-V1 cyanopropylphenyl based phase, 30 mm x 0.53 mm ID x 3.0 μm film and with temperature program 40 °C (hold time 7 minutes), 2 °C/minutes to 80 °C (hold time 3 minutes), 7 °C/minutes to 120 °C (hold time 2 minutes), 15 °C/minutes to 180 °C (hold time 10 minutes).

The *soil samples* (25 g) were centrufugated for 5 minutes at 3000 rpm to remove the excess water. The samples were wetted with 30 mL MeOH/Acetone. The extraction was done with hexane (50 mL) with 20 mL MeOH/Acetone and was shaken manual for 30 minutes at room temperature. The extractions were repeated tree times with hexane.

Identification of the compounds was confirmed by a quadrupole mass spectrometer (DSQ II MS - Termo Electron Corporation) coupled to gas chromatograph (GC) with a split/splitless injector, using the Selective Ion Monitoring (SIM) modality. Cromatographyc separation on GC-MS was achieved using TR-5MS, 5% Phenyl (equiv) Polysilphenylene-siloxane column (Thermo Finnegan, USA). The operation condition is shown in table 4. All injection was done with TriPlus HS autosampler. It working condition are presented in table 4. Quantification was performed using the standard stock solution for organochlorine compounds and based on peak area.

Table 4. GC – ECD, MS-GC and TriPlus HS operation conditions.

MS - GC
Carrier gas flow: helium (He$_2$) 10 mL min^{-1}
Split ratio: splitless
Injector temperature: 200^{0}C
Detector temperature: 300^{0}C
Oven temperature: 40^{0}C (hold time 7 minutes), 2^{0}C/minutes to 80^{0}C (hold time 3 minutes), 7^{0}C/minutes to 120^{0}C (hold time 2 minutes), 15^{0}C/minutes to 180^{0}C (hold time 10 minutes)
Solvent delay: 1.5 minutes
MS scan program: 40 – 750 m/z
Ionization: 70 eV electron impact

GC - ECD
Carrier gas flow: nitrogen (N_2) 30 mL min^{-1} Make up: nitrogen (N_2) 30 mL min^{-1} Split ratio: 1:5 Injector temperature: 200^{0}C Detector temperature: 300^{0}C Oven temperature: 35^{0}C (hold time 3 minutes), 15^{0}C/minutes to 200^{0}C (hold time 3 minutes)
TriPlus HS
Incubation time: 45 min Incubation mode: constant Agitator temperature: 60^{0}C Agitator on – 20 sec/ Agitator off – 20 sec Syringe temperature: 80^{0}C Injection depth: 35 mm Injection speed: 40 mL/min Filling volume: 1.2 mL Filling counts: 1 /Filling delay: 0 sec Post injection syringe flush: 30 sec

The organochlorine compounds after analysis were shown in chromatograms obtain after the water sample analysis on GC-MS – see figure 4.

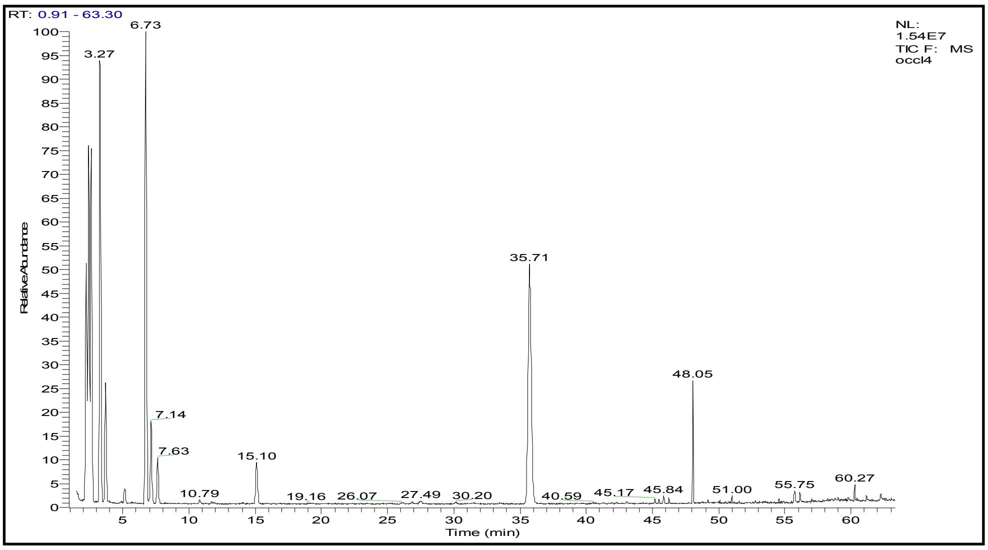


Figure 4. Chromatogram obtained after analysis of water sample on GC-MS with SIM method.

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